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A critical assessment of multifunctional polymers with regard to their potential use in structural applications

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ABSTRACT

Multi Wall Carbon Nanotubes (MWCNTs) and Polyhedral Oligomeric Silsesquioxanes (POSS) are common additives to simultaneously enhance electrical conductivity and flame resistance. In the present work, the synergistic effect of the addition of MWCNTs and two different POSS compounds, DodecaPhenyl POSS (DPHPOSS) and Glycidyl POSS (GPOSS), on the mechanical behavior of multifunctional polymers subjected both to quasi-static as well as to fatigue loading was investigated. The results of the mechanical tests were discussed supported by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) analyses. The results showed that the incorporation of MWCNTs in the resin containing GPOSS determines a slight decrease in the flexural modulus compared to the unfilled resin. The material filled with MWCNTs and DPHPOSS shows a higher reduction of the flexural modulus as compared to the other analyzed materials. The same trend was observed also for the flexural strength; more than 50% decrease of the flexural strength of the material filled with MWCNTs and DPHPOSS is detected. As far as the fatigue is concerned, it seems that the incorporation of the flame retardants led to an appreciable decrease in the fatigue life. The decrease in the mechanical properties of the nanofilled resin loaded with DPHPOSS is most likely due to the presence of aggregates of DPHPOSS crystals in the matrix. This hypothesis is confirmed by EDX analysis which shows that DPHPOSS forms some small aggregates, whereas GPOSS, being molecularly solubilized in the epoxy formulation, shows mechanical performance more similar to the sample loaded only with carbon nanotubes.

1. Introduction

Adding nanocages and/or carbon-based nanoparticles to an epoxy matrix can enhance its multifunctional performance [1–4]. This strategy is particularly effective in yielding high performance composites, when the nanoadditives, such as nanocages and nanoparticles, are well dispersed in the epoxy matrix and the properties of the nanoscale filler are substantially different or better than those of the matrix [3,5,6]. A distribution of nanoadditive at nanoscale level in the composite can offer new physical properties, such as enhancement in the electrical conductivity and fire resistance, which are substantially absent in the unfilled resins, effectively modifying the nature and performance of the original material. Multi Walled Carbon Nanotubes (MWCNTs) and Polyhedral Oligomeric Silsesquioxanes (POSS) are common additives to produce polymers with improved electrical conductivity as well as fire resistance [7–10]; both features are relevant for the design of a variety of applications ranging from simple applications to aeronautics and space applications. Furthermore, CNTS are found to be effective in medicine, as biomaterials in Tissue Engineering, load-bearing implants, and Neuron Engineering [11–13]. In addition, the interaction of POSS compounds with atomic oxygen may enable self-healing capabilities in satellite applications [14].

To take advantage of the improved electrical conductivity and flame resistance and to better understand the field of applicability, there is the need to assess the effect of the additives on the mechanical behavior of the material. In fact, although many studies deal with the effect of MWCNTs or POSS compounds on the mechanical properties of the composites, there is a limited research performed on the simultaneous effect of both additives on mechanical behavior of the composites [3,15]. Researches related to the crack growth rate measurement on double cantilever beam (DCB) specimens made of a carbon-fibre fabric-reinforced multifunctional epoxy composite constituted by GPOSS and MWCNTs embedded in epoxy formulations highlighted relevant benefits from an industrial point of view. In particular, the specimens

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enhanced by CNTs and GPOSS highlighted a significant decrease in the fatigue crack growth rate of approximately 80%. The crack growth rate was also observed to be significantly related to the interface of the weft and warp tows of the plain weave [15,16].

Investigations available in the open literature on the mechanical behavior of composite materials enhanced with both, MWCNTs and flame retardants, remain up to now very limited. In Ref. [17], the effect of both CNTs and flame retardant GPOSS on the mechanical behavior of an epoxy polymer RTM6-2 subjected to several types of quasi-static loading was investigated. The results have shown a significant increase for the tensile strength of the polymers filled only with MWCNTs as compared to the unfilled material. However, the other properties, namely compression, flexural as well as G_{IC} fracture toughness properties were partially decreased. Moreover, Kadlec et al. [18] studied the mechanical behavior of carbon fibre–reinforced epoxy composites enhanced with 0.5 wt % MWCNTs as well as 5 wt % Glycidyl POSS (GPOSS). An approximately 10% decrease on the mechanical properties, namely tensile, three-point-bending, interlaminar shear strength as well as G_{IC} fracture toughness properties was found; the authors assumed that the decrease was associated with possible CNTs agglomerations on the fracture surface of the Double Cantilever Beam (DCB) specimens used in G_{IC} fracture toughness tests.

On the other side, a number of studies about the separate effect of MWCNTs on the mechanical behavior of epoxy polymers have been conducted [19–24]. Zhou et al. [19] investigated the concentration effect of an enhanced with 0.1, 0.2, 0.3 and 0.4 wt % CNTs epoxy on its flexural behavior [25]. The maximum flexural strength increase was observed at a concentration level of 0.3 wt % CNTs. The authors assumed that the increase of the flexural properties is attributed to the mobility restriction of polymer chains under loading due to the presence of the CNTs. On the other hand, at a concentration of 0.4 wt % CNTs, the specimens initially exhibited an increase in their stiffness, yet they failed quickly in terms of both, strength as well as elongation to failure; it was explained by the presence of CNTs agglomerations and the resulting stress concentration. The latter was assumed to have led to crack initiation and, hence, to quick failure. According to Ayatollahi et al. [20], the highest K_{IC} increase was recorded at a concentration of 0.5 wt % of MWCNTs in the resin; further MWCNTs increase tended to decrease the K_{IC} value. Furthermore, the authors found a correlation of the K_{IC} fracture toughness, the tensile properties, as well as the electrical conductivity with the MWCNTs aspect ratio. The results showed a considerable improvement on the fracture toughness at the maximum aspect ratio attributed to a better load transfer due to the increased interface of MWCNTs with the matrix.

Polyhedral oligomeric silsesquioxane (POSS) are hybrid inorganic/organic compounds with an inner inorganic core, which is occupied by the silicon and oxygen components and external organic substituents that make them compatible with most polymers [26].

Open literature works concerning the mechanical behavior of epoxy polymers enhanced with POSS compounds are up to now very limited. In Ref. [27], Jones et al. studied the tensile properties of an epoxy resin containing 1, 3, 5 wt % POSS compounds. The tensile results showed an increase of the yield strength and modulus of the enhanced polymer as the POSS concentration was increasing, which was attributed to the small size of POSS which restricts the mobility of the polymer chains under loading. Moreover, Fina et al. [28] investigated the effect of the addition of three different types of polysilsesquioxanes in a rather different type of resin, a non-structural polypropylene (PP), on its tensile behavior. Methyl (Me)-, vinyl (Vi)- and phenyl (Ph) polysilsesquioxane were blended into the polymer matrix. POSS were loaded into the polymeric matrix at 1.5% and 5% of inorganic fraction. The tensile test results showed an increase in the elastic modulus and the yield stress for the vi-PSS, which retained its homogeneity in the filled state. Due to the presence of micron-sized aggregates of the POSS substituents into the polymer, me- and ph-PSS exhibited a degraded tensile behavior as compared to the unfilled polymer. The authors stated that not only the nature of substituent but also the dispersion of PSS are influencing the mechanical behavior; in particular, a more improved flame resistance as well as tensile behavior was obtained with vi-PSS, which is attributed to the homogeneous dispersion.

All structures are subjected to fatigue loading, leading to failures which are occurred beneath the Ultimate Strength. In Reference [29], the effect of MWCNTs and flame retardant GPOSS on the fatigue behavior of the polymer RTM6-2 was investigated. A slight decrease in the fatigue life was found in the range of the low stress levels, by enhancing the polymer with MWCNTs. On the other hand, a significant deteriorating effect on the fatigue life was observed for the polymer enhanced with both MWCNTs and GPOSS. Scanning electron microscopy and energy dispersive spectroscopy investigation revealed MWCNTs agglomerations. Previous studies [30–32] on the fatigue behavior of epoxy filled only with MWCNTs have shown ambiguous results depending on the level of the MWCNTs dispersion into the epoxy. Loos et al. [30] investigated the effect of the incorporation of 0.19 ± 0.0042 wt % MWCNTs into an epoxy on the tension-tension cyclic fatigue behavior. During the production of the copolymer some large MWCNTs agglomerates were removed. Fatigue tests were performed at a stress ratio of R = 0.1 in the range of 25–50 MPa. The results showed a significant enhancement at the low-stress levels for the filled epoxy system, which was attributed to the crack-bridging and pull-out mechanisms of MWCNTs.

In the present work, the effect of the MWCNTs as well as the synergistic effect of MWCNTs and POSS compounds, namely Glycidyl POSS (GPOSS) or DodecaPhenyl POSS (DPHPOSS) on the mechanical behavior of the polymer RTM6-2 is assessed. The aim is to estimate whether this optimized electrical conductivity and flame resistance have, as a side effect, a negative impact on some of the mechanical properties. The epoxy polymers were subjected to quasi-static loading (flexural, G_{IC} fracture toughness) as well as to fatigue loading. To enable the comparison, the investigation was carried out also for the neat epoxy considered here as 'reference'. Scanning Electron Microscopy (SEM) as well as Energy Dispersive Spectroscopy (EDS) analyses were carried out to support a better understanding of the results obtained from the mechanical tests.

2. Materials

The materials have been prepared by the University of Salerno and Carbures Europe S.A. in the frame of the European project IASS. They have been optimized with regard to electrical conductivity and flame resistance.

The material investigated has been an epoxy polymer enhanced with 0.5% (by wt) MWCNTs and either 5 wt% GPOSS or DPHPOSS. In order to make a comparison feasible, unfilled material has been also used, referred to hereafter as 'reference'. The epoxy matrix formulation is based on a mixture of polifunctional epoxy precursors under the commercial name RTM6-2 [33], which is a two component resin designed to fulfill the requirements of the aerospace industry. The operation service temperatures range from −60 °C up to 120 °C. However, the resin used in this study differs from the commercial one since only one type of hardener is used instead of a mixture of hardeners used in the commercial resin. The CNTs used were NANOCYL NC3100 series thin multi-wall carbon nanotubes, with an average diameter of 9.5 nm and an average length of 1.5 μm. The carbon purity is greater than 95% with a metal oxide impurity lower than 5%. The selected MWCNTs concentration was of 0.5% (by wt). The selected concentration of the MWCNTs has been proved to offer sufficient electrical conductivity to composite structures resulting to an effective dissipation of lightning currents during flight [34–37] while the mixture is characterized by good dynamic mechanical behavior [29]. An ultra-sonication for 20 min has been used in order to achieve a uniform dispersion of 0.5% (by wt) MWCNTs within the epoxy matrix (see Fig. 1). This dispersion method has been chosen among others based on the results of the